

# ATOMIC ABSORPTION SPECTROSCOPY VERSUS ALKALINE FUSION METHOD FOR DETERMINING CHROMIUM IN LEATHER\*

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## ABSTRACT

The utility of the atomic absorption method for measuring the chromium content of chrome-tanned leathers was investigated. Factors considered were: hydrolysis of the sample; the presence of glycine or hydrolyzed hide; the effect of a variety of leather finishes; and finally the repeatability of this method. More than 40 leather samples were analyzed simultaneously by both methods. Statistical evaluation of the data indicated a highly significant correlation between the two methods. The presence of glycine or hydrolyzed hide powder did not interfere with the atomic absorption measurements. A test of the repeatability of the atomic absorption analysis was made using a simple chrome-tanned leather sample and a commercially tanned and treated leather. Results indicate that the atomic absorption method as described is reliable and affords a considerable saving of time in determining chromium content of leather.



## INTRODUCTION

The American Leather Chemists' official alkaline fusion method (1) for determining the chromium content of chrome-tanned leather is time consuming. This fact has prompted the investigation of a number of less cumbersome methods for measuring chromium levels in leather. Iida and Fuwa (2) studied a multi-channel flame spectrometric method in which the emissivity of chromium was measured. Montagut *et al.* (3) were the first to apply atomic absorption spectroscopy to the determination of chromium in leather. Their method utilized a wet ashing technique which employed  $\text{HNO}_3\text{-H}_2\text{SO}_4$  as the hydrolyzing mixture and subsequent analysis of the resulting solution. They studied a number of factors, including the oxidation state of the chromium, flame characteristics, and interference due to sodium and calcium. Scroggie, in a recent publication

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(4), reported that he measured the chromium uptake in leather by atomic absorption analysis. However, in all these reports no data are offered showing the reliability of the atomic absorption method when compared to the standard alkaline fusion method. The following study was undertaken to establish the reliability of the atomic absorption method.

#### EXPERIMENTAL

The major portion of the leather samples used in this study were chrome-tanned in our engineering laboratory as part of a general investigation of the tanning process. The usual commercial tanning procedures were followed, using Tanolin R<sup>†</sup> as the source of chromium. Seven additional samples representing a variety of commercially tanned leathers also were analyzed.

All samples were prepared identically, then divided and analyzed concurrently by each method. The sample preparation consisted of air drying the leather strips at 80°C. for 24 hours, then grinding in a Wiley Mill, allowing several passes through a ten-mesh screen to facilitate mixing. The ground leather was dried a second time in a vacuum oven at 70°C. for 16 hours.

For the atomic absorption method, approximately 100 mg. of the dried leather was accurately weighed into a 125 ml. glass-stoppered Erlenmeyer flask containing 25 ml. 2N HCl. Hide powder was washed from the sides of the flask with a small volume of water and the flask was then attached to a cold water condenser and allowed to reflux for four hours. The hydrolyzed sample was cooled slightly, then filtered through Whatman #1 filter paper into a volumetric flask. The filter paper was washed repeatedly with hot de-ionized water to insure quantitative transfer of chromium. The flask volume was chosen so that the concentration of chromium for atomic absorption measurement was at least 2  $\mu\text{g./ml.}$  and did not exceed 25  $\mu\text{g./ml.}$  After cooling to room temperature, the solution was made to volume and aspirated into the air-acetylene flame of the atomic absorption spectrometer.

The remaining portion of each sample was analyzed following the standard alkaline fusion method. All the chemicals and standards used in this analysis were reagent grade.

A Perkin-Elmer Model 303 Atomic Absorption Spectrometer was used for all absorption measurements. Instrument settings and fuel flow rates used were those outlined in the Model 303 manual. Owing to the flame sensitivity of chromium atoms, care must be taken to insure a source of air which is both clean and dry. A single slot burner was used with the aspiration rate maintained at about 2.70 to 3.00 g. solution per minute. Chromium standards containing from 2.0 to 25.0  $\mu\text{g.}$  chromium per ml. were prepared from a certified atomic absorption standard solution (Fisher Scientific Co.) containing 1000 p.p.m. chromium.

<sup>†</sup>Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

The bracketing technique was used for determining chromium concentration of each sample, with the sequence of absorption measurement being standard A, sample, standard B. The sequence was followed a minimum of two times for each sample. Standards A and B differed in chromium concentration by 5  $\mu\text{g./ml.}$  or less.

#### RESULTS AND DISCUSSION

The initial comparison of the two methods under study was done on 35 samples of chrome-tanned leather which were analyzed in duplicate. The samples were divided after final drying and analyzed following the procedures described. Although tanned leather usually contains about four percent  $\text{Cr}_2\text{O}_3$  on a moisture-free basis (MFB), these samples ranged from 2.80 to 11.00 percent  $\text{Cr}_2\text{O}_3$  (MFB), thus permitting a broader evaluation of the atomic absorption method. The results of this comparative study are plotted in Figure 1, which gives percent

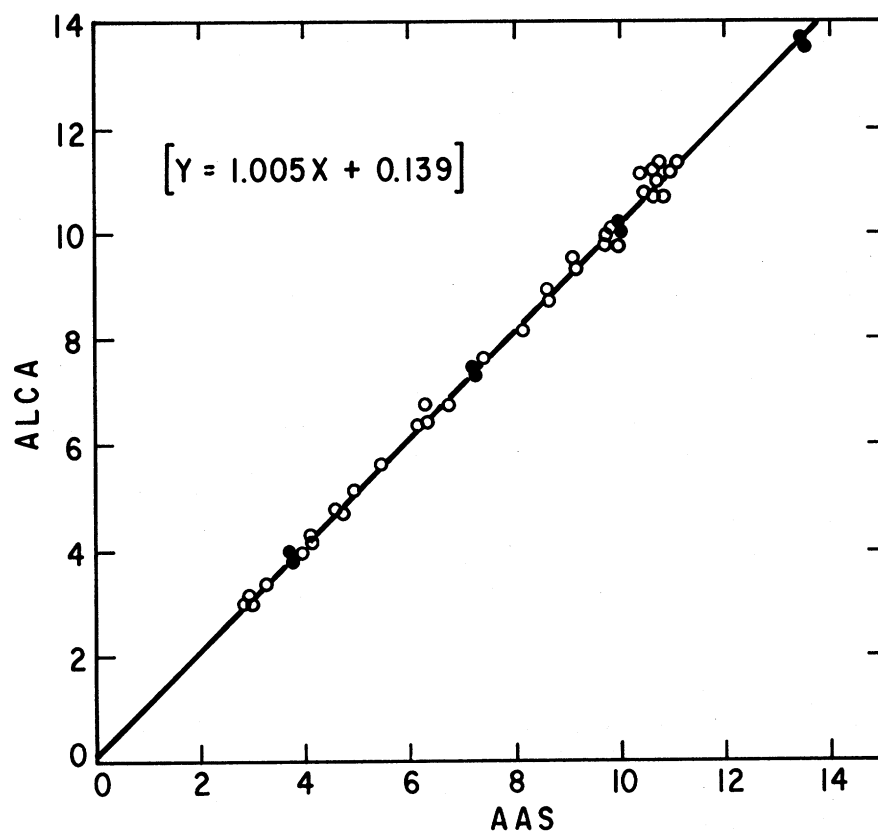


FIGURE 1.—Percent  $\text{Cr}_2\text{O}_3$  as determined by both methods. (Values are the average of duplicates.)

Cr<sub>2</sub>O<sub>3</sub> in leather as determined by the standard versus the percent Cr<sub>2</sub>O<sub>3</sub> as determined by the atomic absorption method. A linear regression and an analysis of variance (ANOVA) of these data indicate that a highly significant linear relation exists between the results obtained by each method. The slope of the line is 1.005, thus indicating that the methods gave essentially identical results.

The standard deviation (5) of each method was determined from the duplicate values, using the equation

$$\text{S.D.} = \sqrt{\frac{\sum d^2}{2n}}$$

where S.D. = standard deviation; d = difference between each set of duplicates; and n = number of duplicates. The results shown in Table I indicate that the standard deviation for the duplicates by the atomic absorption method (0.105) is higher than the same statistic for the alkaline fusion method (0.034). Also in

TABLE I  
STATISTICAL EVALUATION OF THE COMPARATIVE DATA

Method	n	Std. Dev.	F
AAS	35	0.105**	9.54*
ALCA	35	0.034	

\*Significant difference at 99% probability level.

\*\*% Cr<sub>2</sub>O<sub>3</sub> (moisture-free basis).

Table I, the ratio of the variance (F value) for the data is shown, indicating a significant difference between methods. However, although the standard deviation for the atomic absorption data is somewhat greater than the data obtained by the standard fusion method, the atomic absorption method is sufficiently precise for most purposes at the levels of chromium (four to six percent) normally encountered in commercial leathers.

The two methods also were compared using a series of samples that typify a variety of commercially prepared leathers. These samples were prepared and analyzed as described above. The atomic absorption results, although lower (Table II), are almost identical with the fusion values [avg. diff. = -0.126 percent Cr<sub>2</sub>O<sub>3</sub> (MFB)].

Although the difference between results obtained by the two methods is minimal, a number of factors potentially responsible for this difference were studied.

Montagut indicated no difference in atomic absorption of the two oxidation states of chromium; nevertheless, it was decided to verify this fact, especially since the acid hydrolysis yields Cr<sup>+3</sup> and the standard solutions used are Cr<sup>+6</sup>. Various leather samples were analyzed for chromium by the absorption method,

TABLE II  
COMPARATIVE DATA FOR A VARIETY OF LEATHERS  
% Cr<sub>2</sub>O<sub>3</sub> (MOISTURE-FREE BASIS)

Sample	ALCA	AAS
Patent Leather	3.48 3.36	3.35 3.18
Chrome-Tanned, Glutaraldehyde- Retanned, Silicone Treated	4.76 4.73	4.70 4.76
Kenabago Crust, Chrome and Vegetable Retanned	3.13 3.16	2.92 2.91
Kenabago Finished, Chrome and Vegetable Retanned	3.06 3.01	2.89 2.79
Chrome- Glutaraldehyde Tanned, Unfinished	3.99 4.00	3.99 3.90
Chrome- Glutaraldehyde Tanned, Finished	4.23 4.24	4.15 4.06
Chrome-Tanned, Glutaraldehyde and Vegetable Retanned	3.04 3.06	2.99 2.90

using both CrCl<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solutions as standards. The results, which are consistent with Montagut's findings, showed no difference due to the oxidation state of the chromium.

The effect of hydrolyzed hide powder or the amino acid glycine on the atomic absorption response also was investigated. A series of standard solutions were prepared, containing 50 or 100 mg. of glycine or 100 mg. of hide powder. The ready solubility of glycine in the aqueous standards permitted atomic absorption measurements with and without acid hydrolysis. However, the standard chromium solutions containing hide powder could be prepared only following the acid hydrolysis procedure. The atomic absorption of these model solutions was compared with the absorption of the regular standards. Shown in Figure 2 are the results of the absorption measurements for a 15 µg./ml. chromium solution with and without hydrolyzed hide powder obtained over a 21-day period. Similar results (not shown) were obtained with a ten and a 20 µg./ml. standard solution. Although not shown, identical results were obtained for the standard solutions containing glycine. These results show little difference between the two systems and indicate that the presence of breakdown products of acid hydrolyzed hide will not interfere with the atomic absorption measurements.

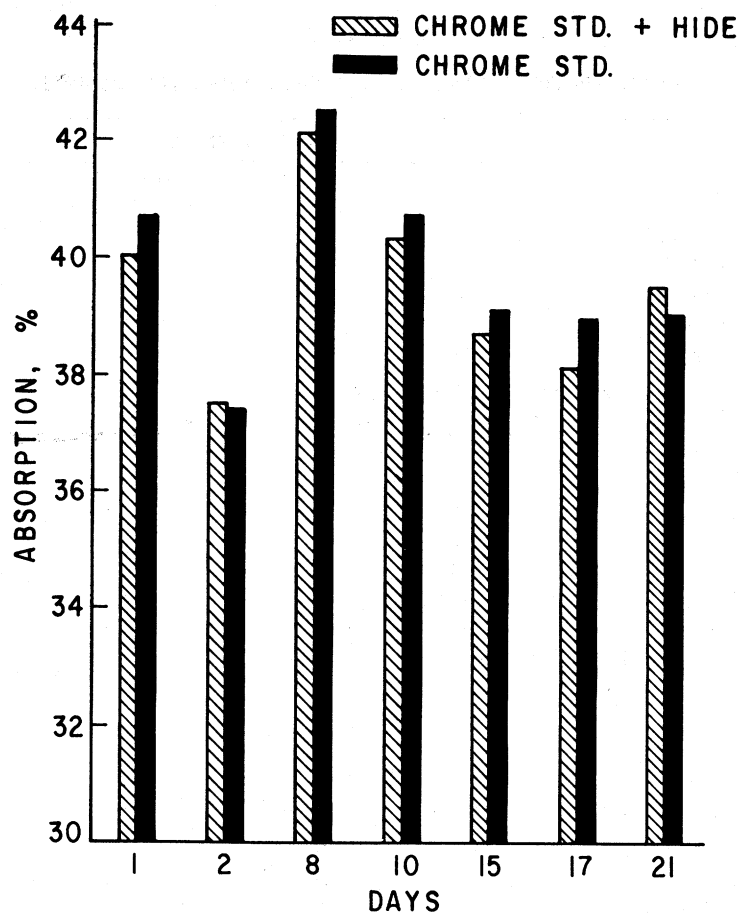


FIGURE 2.—Absorption of chromium standards with and without hydrolyzed hide powder.

Finally, statistical analysis was performed on a pool of atomic absorption data obtained for two samples representing the simple chrome-tanned hides as well as a commercial leather. The commercial leather was chrome-tanned, glutaraldehyde and vegetable retanned. This statistical analysis is designed to indicate the precision of the method under evaluation by revealing both a within-day as well as the day-to-day variance. The pooled data were obtained by analyzing the samples in quadruplicate each day on four separate days.

The raw data, along with an analysis of variance for each sample, are shown in Tables III and IV. Both samples showed little within-day variation. The ANOVA for the leather sample containing 3.18 percent  $\text{Cr}_2\text{O}_3$  (Table III) also shows no significant day-to-day variation (F value =  $<1.0$ ). In Table IV, however, the ANOVA for the second leather sample (6.87 percent  $\text{Cr}_2\text{O}_3$ ) does have a significant F value (16.038), thus indicating the existence of a day-to-day

TABLE III  
ANALYSIS OF VARIANCE OF SINGLE LEATHER SAMPLE

Sample	% Cr <sub>2</sub> O <sub>3</sub> (MFB*)			
	Day 1	Day 2	Day 3	Day 4
Chrome Tanned,	3.25	3.20	3.22	3.19
Glutaraldehyde	3.19	3.12	3.19	3.20
and Vegetable	3.18	3.16	3.13	3.17
Retanned	3.15	3.23	3.15	3.14
Mean:	3.19	3.18	3.17	3.18

Grand Mean = 3.18% Cr<sub>2</sub>O<sub>3</sub> (MFB\*)

Variation from Grand Mean =  $\pm 0.07\%$  Cr<sub>2</sub>O<sub>3</sub>

ANOVA

Source	SS	dF	MS	F
Total	0.0201	15		
Days	0.0009	3	0.0003	<1.0
Replicates	0.0192	12	0.0016	

\*MFB = moisture-free basis.

TABLE IV  
ANALYSIS OF VARIANCE OF SINGLE LEATHER SAMPLE

Leather Sample	% Cr <sub>2</sub> O <sub>3</sub> (MFB*)			
	Day 1	Day 2	Day 3	Day 4
Chrome-Tanned	6.74	6.86	7.03	6.95
	6.66	6.68	7.08	6.98
	6.76	6.82	6.95	6.94
	6.74	6.80	6.88	7.02
Mean:	6.73	6.79	6.98	6.97

Grand Mean = 6.87% Cr<sub>2</sub>O<sub>3</sub> (MFB\*)

Variation from Grand Mean =  $\pm 0.21$

ANOVA

Source	SS	dF	MS	F
Total	0.2556	15		
Days	0.2045	3	0.06816	16.038**
Replicates	0.0511	12	0.00425	

\*MFB = moisture-free basis.

\*\*Significant day-to-day variation.

variation. Even though the statistical analysis indicated that the atomic absorption values for the second sample do vary between days, the magnitude of the variation is not excessive.

Since completion of this initial phase of our investigation, a triple slit burner head has been substituted for the single slit unit used throughout this study. Also, every precaution to ensure the availability of a moisture-free air supply to the flame has been taken. The result, thus far, has been better flame stability plus greater reproducibility of the absorption values.

### CONCLUSIONS

The atomic absorption method is a rapid and reliable method for determining chromium in leather. The oxidation state of the chromium atom is not a factor; thus direct chromium analysis of both leather and the tanning solution may be carried out without prior oxidation or reduction. Neither glycine nor acid hydrolyzed hide interfere with this determination. A statistical study indicated that the atomic absorption data had confidence limits ( $\rho = 0.05$ ) of  $\pm 0.197$  percent  $\text{Cr}_2\text{O}_3$ , compared to  $\pm 0.065$  percent for the alkaline fusion method.

### ACKNOWLEDGMENT

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### DISCUSSION

MR. BATTLES: The discussion leader for this paper will be Dr. Thorstensen.

DR. THORSTENSEN (Thorstensen Laboratory): Mr. DellaMonica has conducted a real workmanlike job in the comparison of two methods of chromium analysis. The alkaline fusion method is certainly tedious and time-consuming, and therefore one that's not done for most routine chemical work in tannery laboratories.

In both the perchloric acid digestion method and the alkaline fusion method gross errors can result in the chromium determination from relatively small variations in the analyst's technique.



The atomic absorption spectroscopy method is certainly convenient and has been shown to be sufficiently accurate for routine research purposes. It wouldn't be fair to let this pass without saying that such sophisticated equipment is unfortunately not available to most leather research laboratories, and is certainly not available for the usual tannery laboratory.

Atomic absorption spectroscopy is related, to some degree, to flame photometry. Many of us have played with flame photometry for the determination of chrome and given it up because of the interference of other ions. Sodium and calcium ions would cause enough background light so that the flame photometry method could not be used for chromium with consistent accuracy.

I'd like to ask Mr. DellaMonica about this. Does the atomic absorption spectroscopy eliminate this difficulty, and if so, is it possible to determine several elements from the same sample?

MR. DELLAMONICA: In atomic absorption this is the advantage, in comparison with flame photometry. You don't have spectral interference due to the other ions that are in solution. The fundamental difference between the two techniques is that in flame photometry you're using the flame as your primary source of radiation. In atomic absorption, the hollow cathode tube which is housed in the instrument is the source of radiation, and it is highly specific. The cathode is made of the metal element that you are interested in; for example, in our case we are using a chromium lamp. Because chromium is very difficult to handle as a metal, the cathode is a copper shell that has been chromium plated. Therefore, the radiation emitted from this lamp is characteristic of both copper and chromium.

Incidentally, if you ever run atomic absorption with chromium lamps, they make very excellent copper lamps also. All that is required is changing the monochrometer to pick out the proper resonance line for copper, and you can run copper solutions also.

So, you see, you're not depending on the emission of energy from the flame. You're really depending on the emission of energy from your hollow cathode tube. The difference also is that in flame photometry you're measuring only the atoms that have been excited and that are on their way down from the excited state. In atomic absorption, it's the other way around. You're measuring ground state atoms that are on their way up.

I recently read that with sodium, which gives a rich orange flame, only three percent of the atoms were excited; this gives you some idea of how many atoms were still in the ground state.

MR. DONOVAN (Canada Packers Limited): In your regression line, correlating atomic absorption with alkaline fusion, you had a positive intercept. Was that intercept statistically significant, and if so, to what do you attribute it?

MR. DELLAMONICA: We were bothered by this also. It was not statistically significant. We played with the statistics a little bit and found that the regression analysis that was corrected for the mean of these data, caused the line to tilt somewhat.

DR. THORSTENSEN: If there are no further questions, I wish to thank Mr. DellaMonica for an interesting presentation.